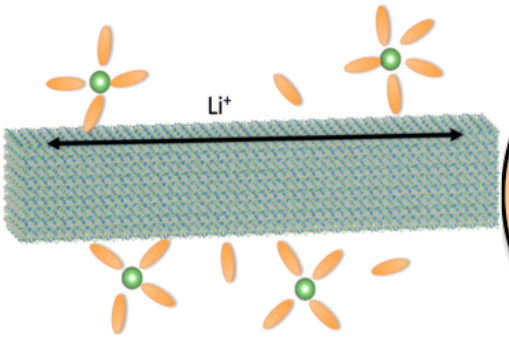
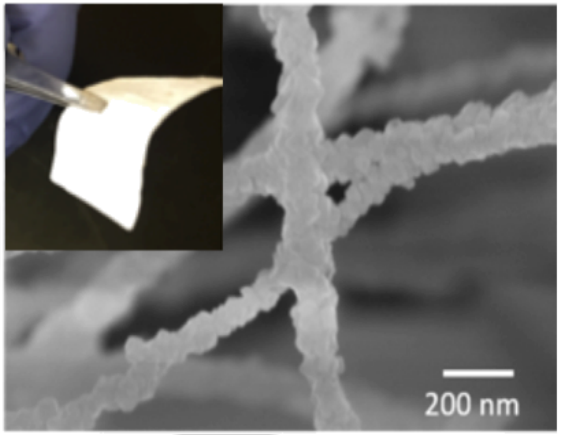
High Conductivity and Flexible Hybrid Solid State Electrolyte

Eric D. Wachsman, Liangbing Hu, Yifei Mo



MO (Computation):
- Mechanical flexibility;
- Ion transport on surface and interface;
- Li metal dendrite;
- Interface impedance.



WACHSMAN (Experiment):
- Nanofibers with optimized garnet composition, process and dimensions;
- FIB/SEM structures

Flexible, Solid State Hybrid Electrolyte

HU (Experiment):
- Hybrid electrolyte
- Li metal anode with hybrid electrolyte;
- Li-S cells with hybrid electrolyte.

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Project ID: ES322

Overview

Timeline

- Project Start: October 1, 2016
- Project End: September 30, 2019
- Percent Complete: 20%

Budget

- Total Project Funding: $1,388,889
  - DOE Share: $1,250,000
  - Cost Share: $138,889
- FY 2016 Funding received: $1,250,000

Barriers

- Solid state batteries are known for high bulk and interfacial impedance and are inherently rigid
- Organic electrolytes are less stable, flammable, have limited mechanical strength and ability to block dendrites
- A balance is needed which combines the advantages of both types of electrolytes to enable “beyond Li” batteries

Partners

- Longstanding collaboration with Prof. Venkataraman Thangadurai

Relevance

Objectives

- Develop high-conductivity (>0.5 mS/cm), flexible, low-interfacial impedance garnet-organic hybrid electrolytes based on garnet nanofibers.
- Demonstrate Li-S batteries with ~450 Wh/kg for 500 cycles

Impact

- A hybrid flexible solid electrolyte will enable high-energy density, safe Li metal batteries with 2-3X energy density that can still be processed within existing battery manufacturing infrastructure

Milestones and Approach

Approach

Use computational modeling and experiment to

- Determine Li diffusion, Li dendrite protection, and mechanical properties of garnet, polymer electrolytes, and hybrid electrolytes
- Characterize electrochemical, mechanical, and thermal properties of hybrid electrolytes
- Optimize hybrid electrolyte and produce full cell Li-S battery delivering 450 Wh/kg for 500 cycles

		Year 1				Year 2				Year 3			
	Name(Task, Subtask, Milestone)	Q 1	Q 2	Q 3	Q 4	Q 5	Q 6	Q 7	Q 8	Q 9	Q 10	Q 11	Q 12
1	Task 1: Develop computational models												
2	Task 2: Synthesize and characterize garnet nanofibers												
3	Task 3: Fabricate hybrid solid state electrolyte												
4	Task 4: Determine structure and properties of hybrid electrolyte												
5	Task 5: Li-hybrid electrolyte interface												
6	Task 6: Fabricate and test Li-S full cells												

Q1 Milestone: Fabricate 4 cm x 4 cm garnet nanofiber membrane (**Complete**)

Q2 Milestone: Synthesize ion conductive, insulating and *in situ* synthesized polymer electrolyte coated garnet nanofibers (**Complete**)

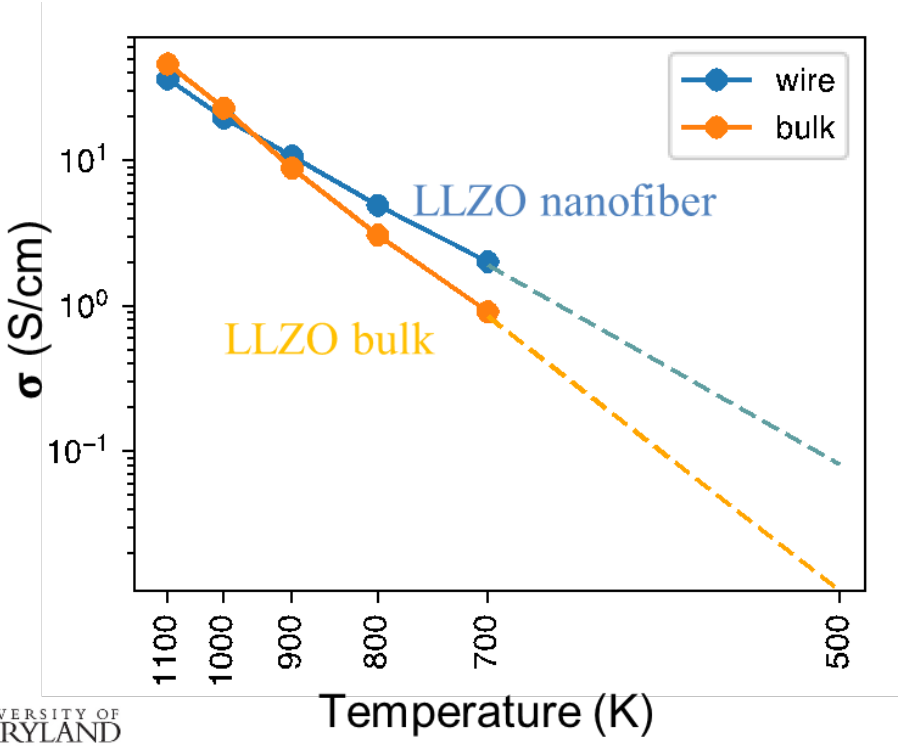
Modeling of Li ion Diffusion in Garnet Nanofibers

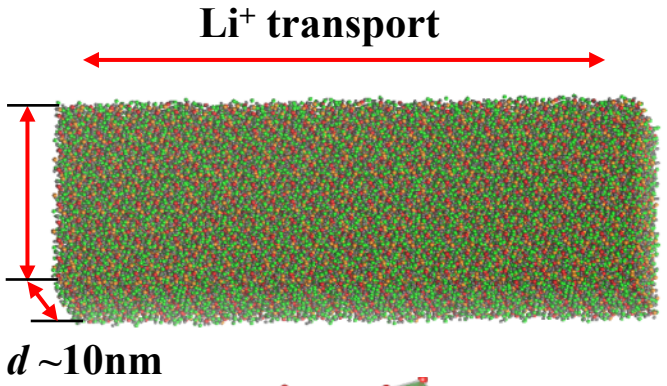
In order to perform large-scale molecular dynamics (MD) simulations for garnet nanofibers, we:

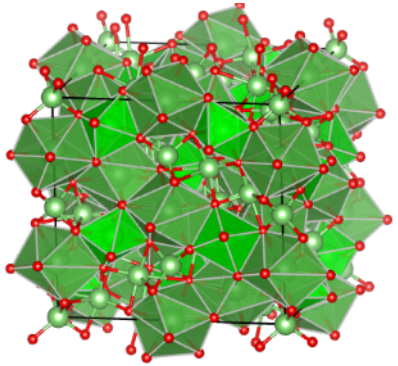
- Benchmark MD force fields for bulk phase LLZO garnet, showing good agreement with experimental values. Demonstrated capability to model large system size.

  MD simulation: $\sigma_{RT} = 1.4$ mS/cm, $E_a = 0.25$ eV;

  Experimental values: $\sigma_{RT} = 0.4$ mS/cm, $E_a = 0.26$ eV
- Preliminary nanofiber modeling showing enhancement in Li ionic conductivity. The mechanism of diffusion enhancement is being investigated.

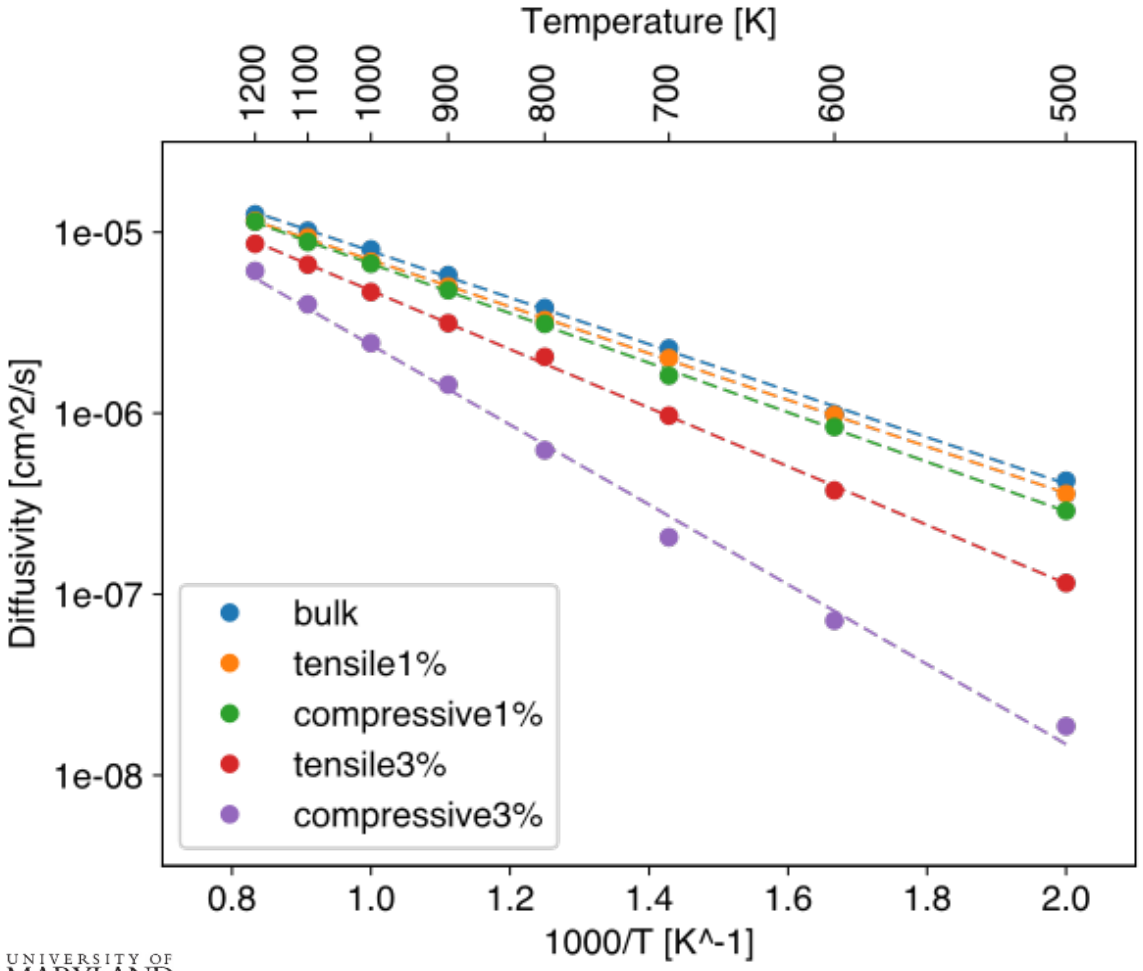






Li^+ Diffusion Under Mechanical Deformation

- Mechanical deformation has significant impact on Li^+ diffusion in garnet.
- Deformation may significantly decrease Li^+ ionic conductivity in garnet. Both tensile and compressive deformation drives garnet towards lower-conducting tetragonal phase.



Cubic-phase garnet

Tensile deformation

Compressive deformation

Develop Hybrid Garnet/Organic Cells - Electrospun Fibers

PNAS

Flexible, solid-state, ion-conducting membrane with 3D garnet nanofiber networks for lithium batteries

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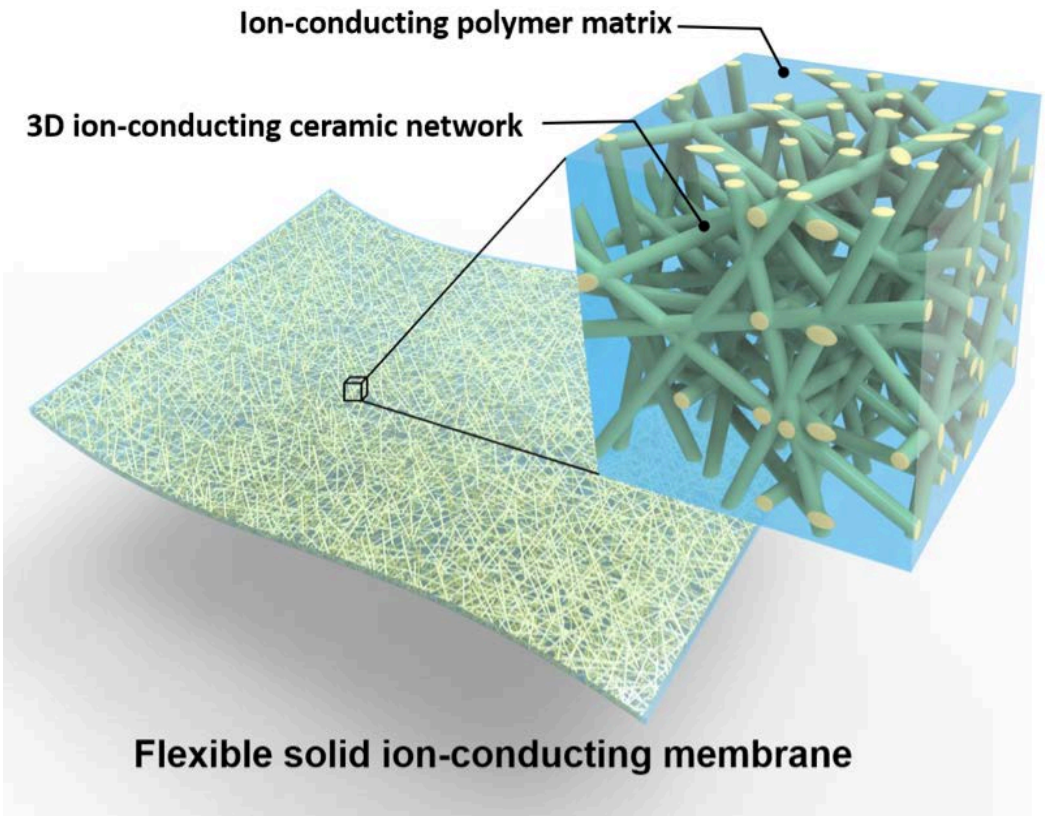
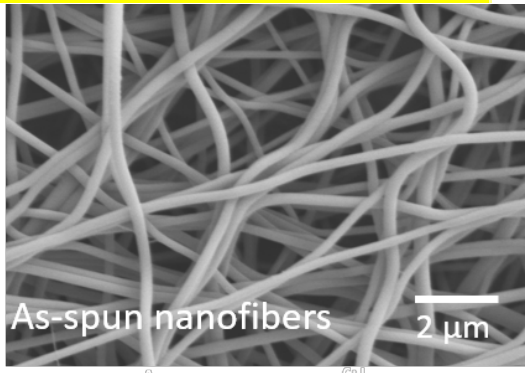
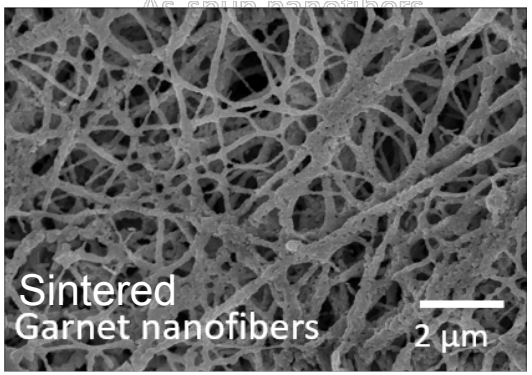
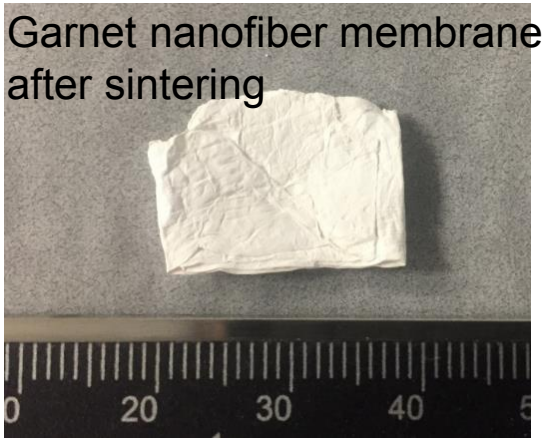






Garnet nanofiber membrane after sintering



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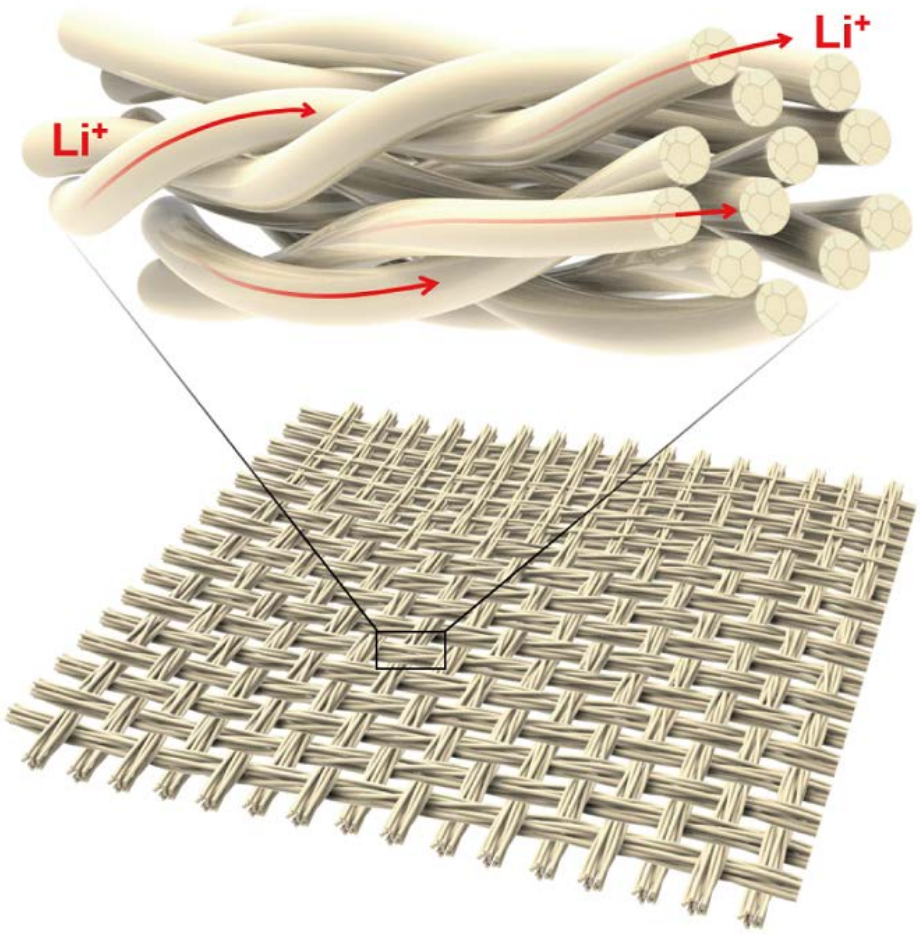
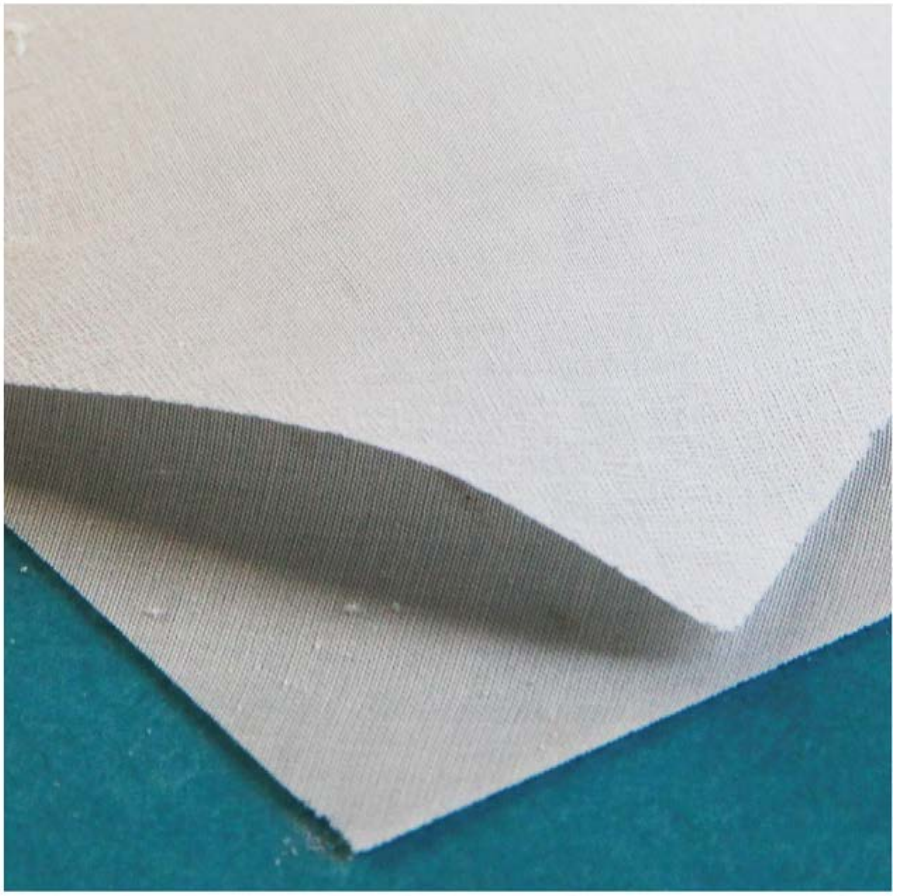
Develop Hybrid Garnet/Organic Cells - Templated

Design of fibrous garnet textile





- Lithium ion conductive.
- Low gravimetric density.
- High surface area/volume ratio.
- Flexible.

Develop Hybrid Garnet/Organic Cells - Templated

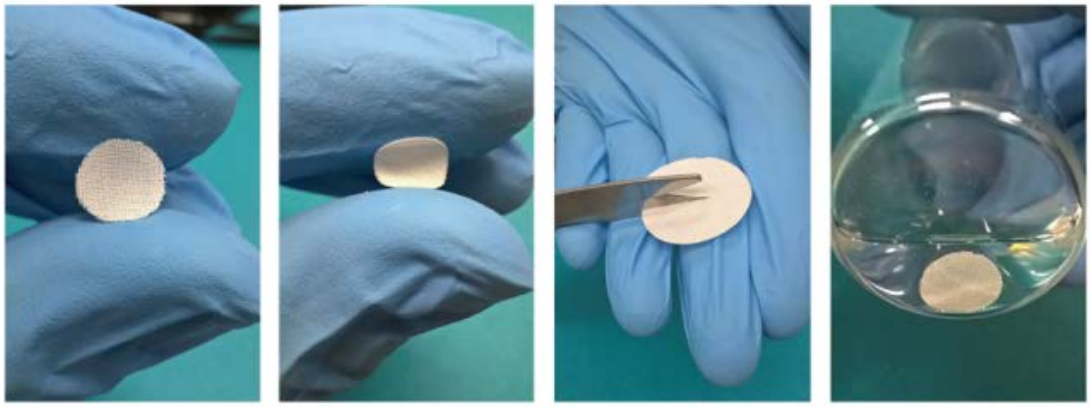
Template replica fabrication process

Textile template

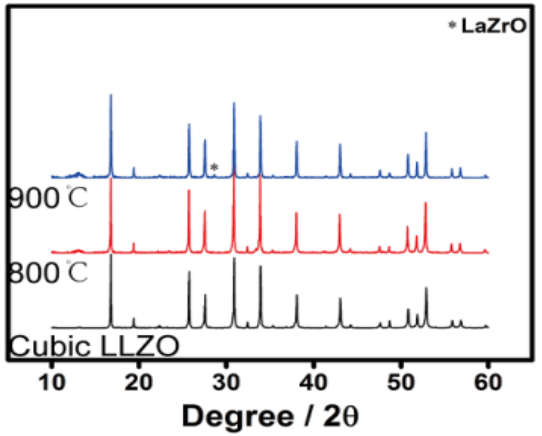
Precursor impregnated textile template

Garnet textile

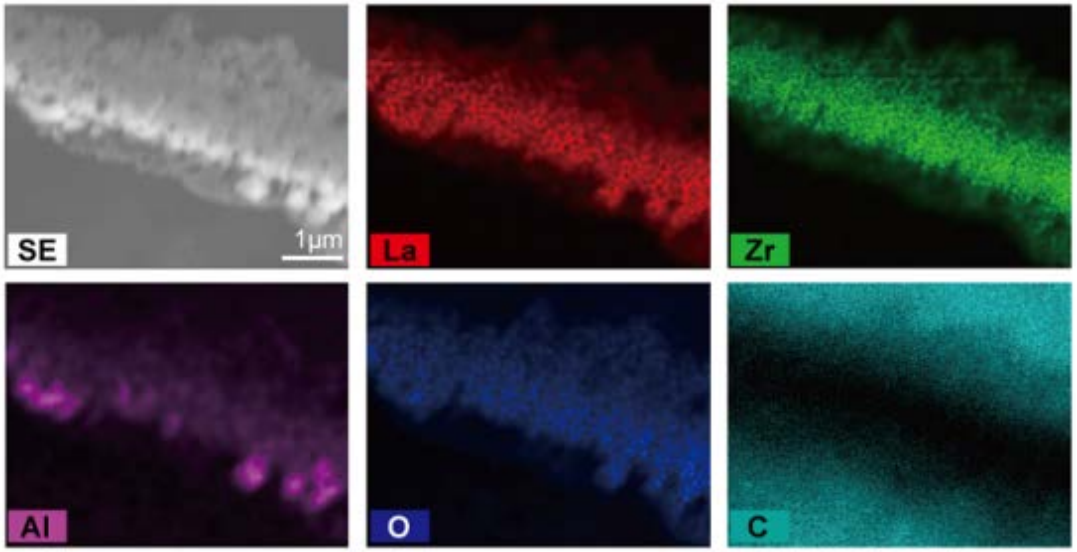
Develop Hybrid Garnet/Organic Cells - Templated



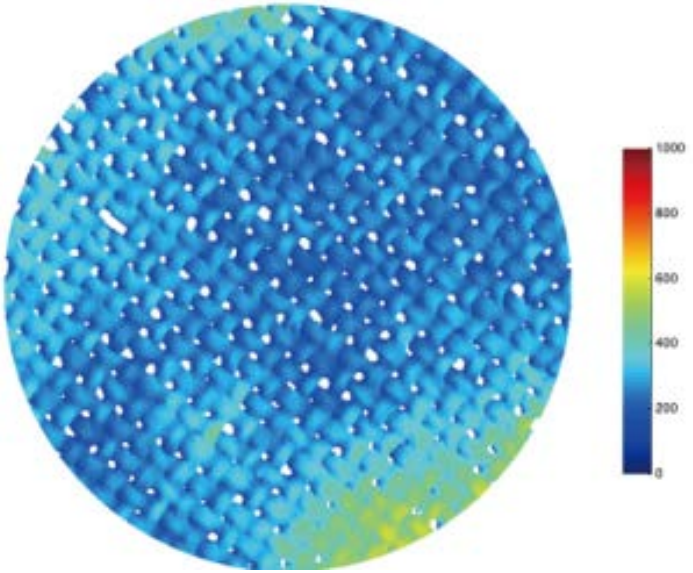
Flexibility and workability



Demonstrated Cubic phase



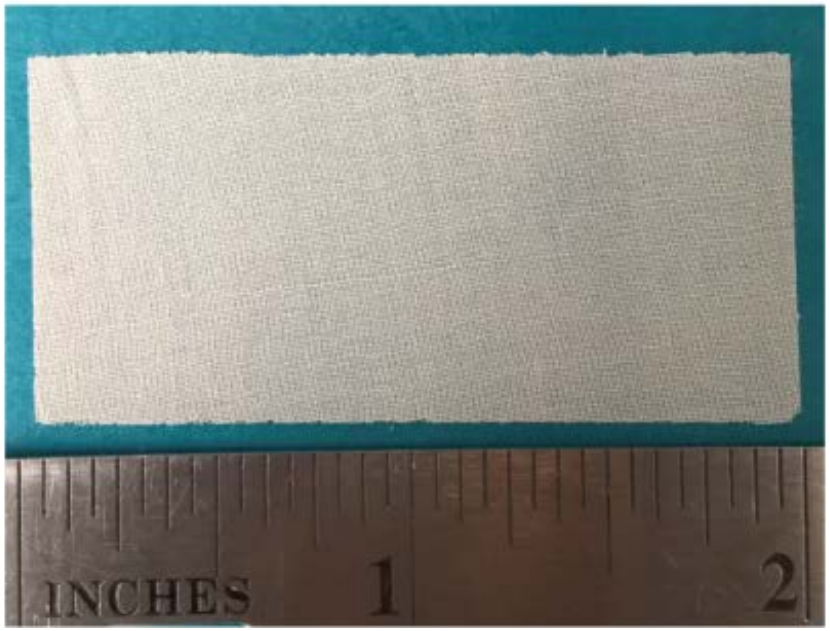
Elemental distribution demonstrating garnet composition

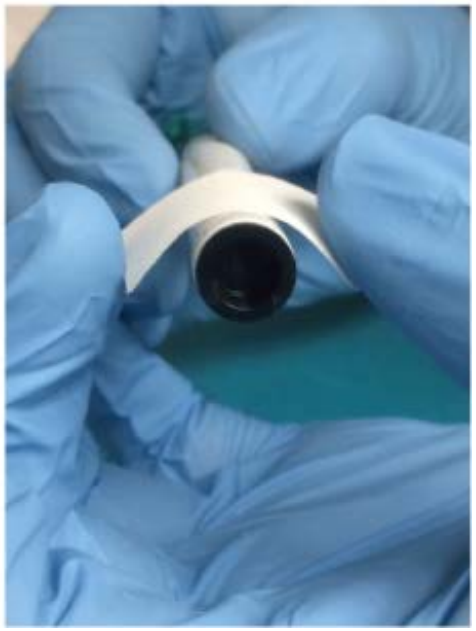


Demonstrated flatness

Develop Hybrid Garnet/Organic Cells - Templated

Simple, Rapid, Low-cost, Scalable fabrication of garnet textile



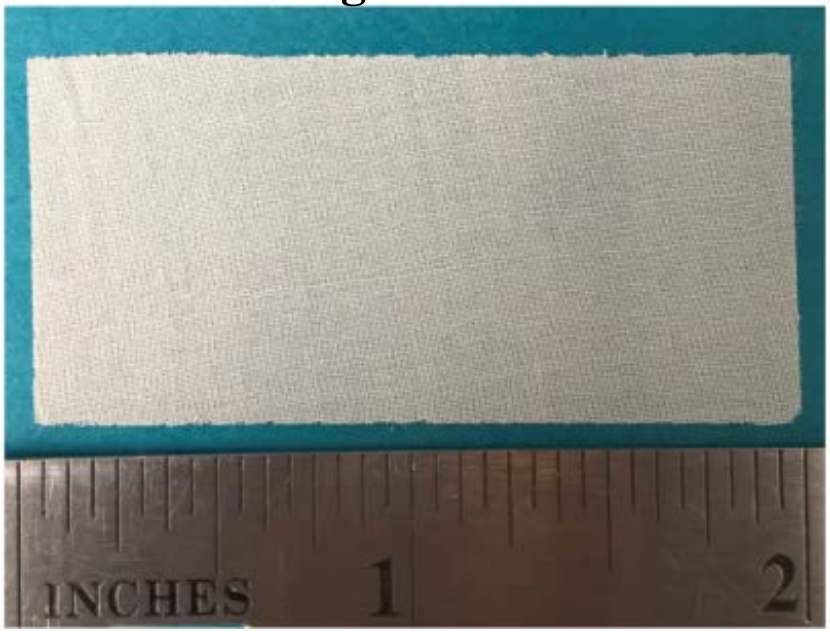


- Low gravimetric density.
- Flexible.

Q1 Milestone - Fabricate 4 cm X 4 cm garnet fiber mat

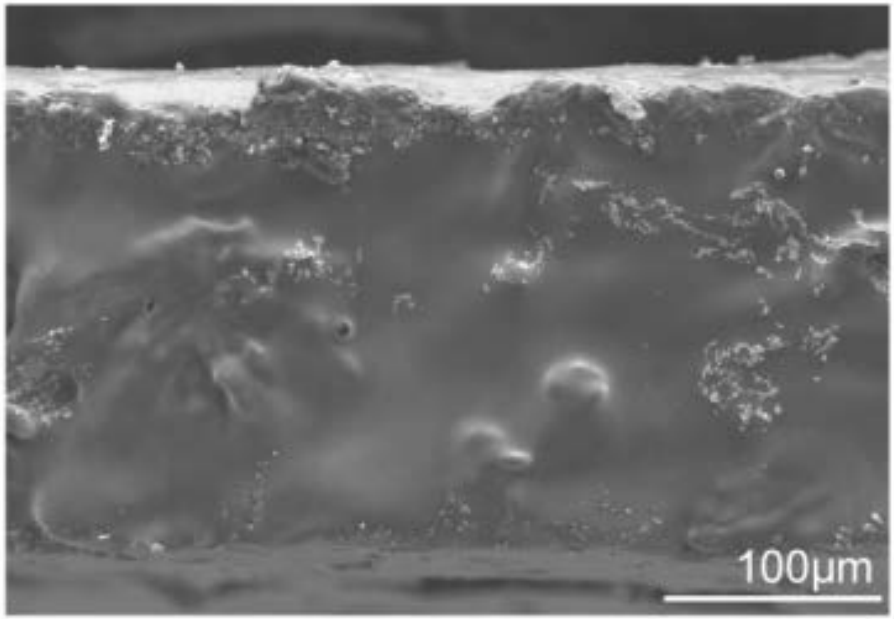
Develop Hybrid Garnet/Organic Cells - Templated

Simple, Rapid, Low-cost, Scalable fabrication of garnet textile



- Low gravimetric density.
- Flexible.

Garnet textile reinforced Hybrid Composite Polymer Electrolyte

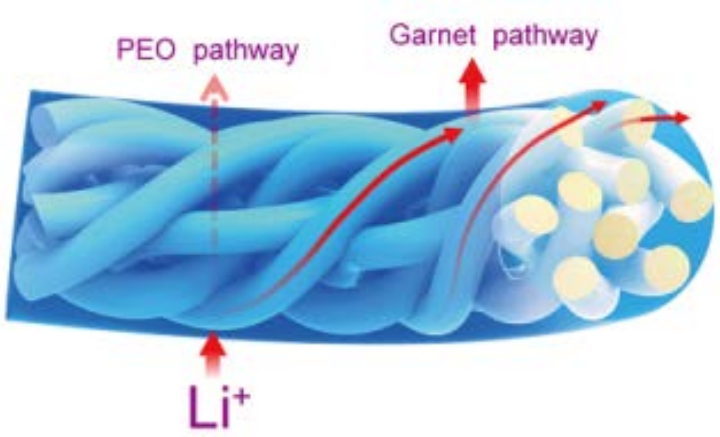


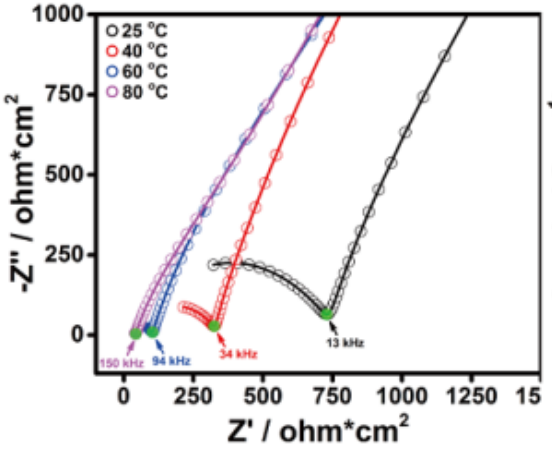
- Lithium ion conductive.
- Dense and free of pores.

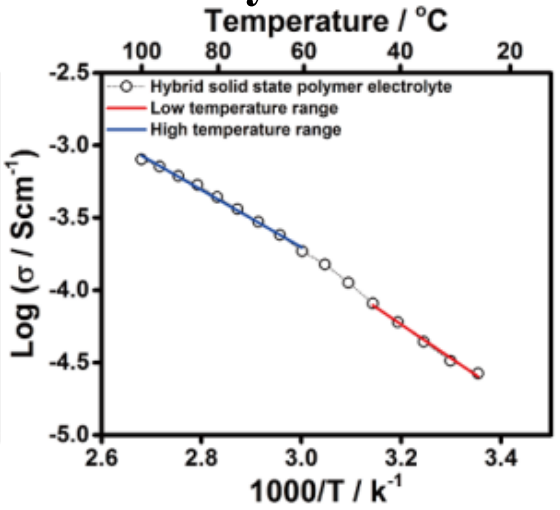
Q2 Milestone - Synthesize polymer electrolyte coated garnet fibers

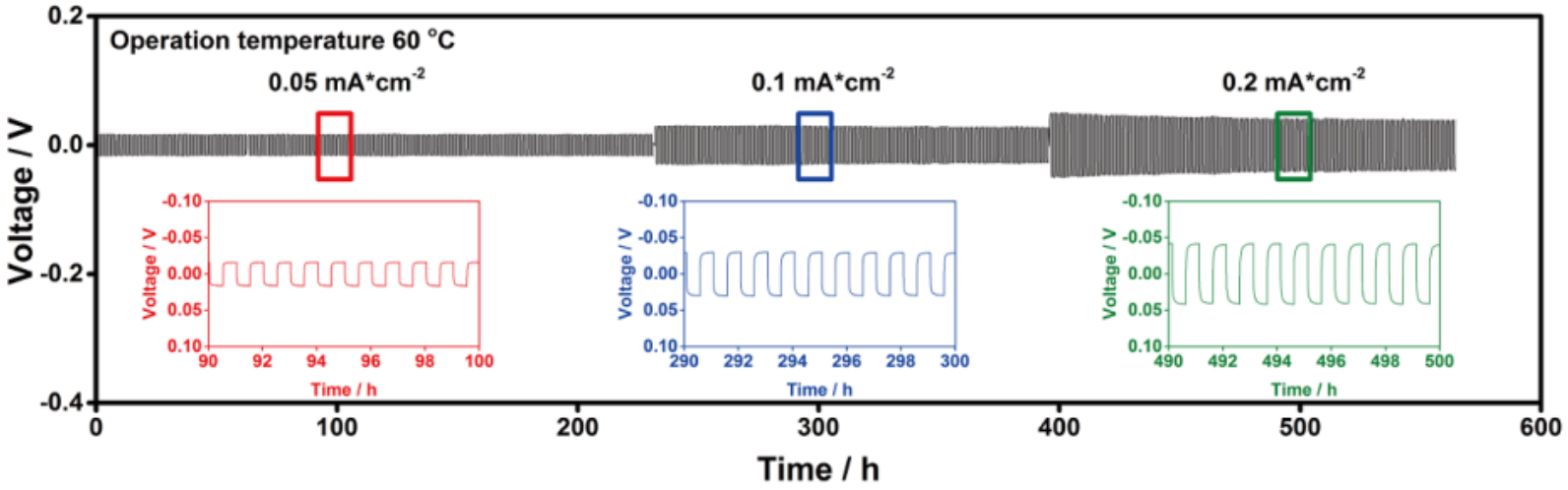
Develop Hybrid Garnet/Organic Cells - Templated

Lithium ion conduction within
garnet textile reinforced Composite Polymer Electrolyte









Stable cycling of polymer electrolyte coated garnet fibers

Response to Previous Year Comments

This project was not reviewed last year.

Collaboration and Coordination

Continued collaboration with Prof. Venkataraman Thangadurai
University of Calgary (co-inventor of garnet)

Remaining Challenges and Upcoming Work

- Reaching high conductivity goals (0.5 mS/cm) requires optimization of hybrid electrolyte
- Improved models are needed to understand how to prevent Li dendrite growth while increasing Li conductivity
- Reducing templated hybrid electrolyte thickness to 20 μm necessitates further process modifications

Proposed Future Research

FY17
- Model ion diffusion in garnet nanofibers
- Characterize nanoscale mechanical properties and boundary impedances
- *In situ* synthesis of polymer electrolyte coated garnet nanofibers.

FY18
- Include mechanical response of nanofibers in model
- Full characterization of hybrid electrolyte, including microstructure, electrochemical, mechanical, and thermal properties
- Fabricate < 20 μm electrolyte and determine Li/electrolyte interface up to 3 mA/cm^2

FY19
- Fabricate porous framework with mixed electron/ion conductivity
- Demonstrate Li-S cells with 450 Wh/kg

Any proposed future work is subject to change based on funding levels.

Summary

- Developed multiple approaches to make flexible hybrid polymer/garnet fiber electrolyte membranes:
  - Electrospun nanofibers
  - Templated fiber mats
- Fabricated flexible and scalable 4 cm X 4 cm garnet fiber mat (Q1 Milestone)
- Synthesized polymer garnet fiber hybrid electrolyte with good conductive properties (Q2 Milestone)
- Developing fundamental understanding of Li diffusion in garnet nano fibers and response to mechanical deformation (Q3 Milestone)